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(54) TREATMENT OF ZIRCONIUM AND ITS ALLOYS BY CHEMICAL DISPLACEMENT

(71) We, EUROPEAN ATOMIC ENERGY COMMUNITY (EURATOM), 51—53, Rue Belliard, Brussels, Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method of treating the surfaces of zirconium and its alloys by chemical displacement. Such treatment may be, but is not necessarily, employed as a preliminary to plating with another metal.

As is known, zirconium and its alloys, like many other substances, have their surfaces covered with very tough, compact passivation layers, with the result that surface treatment and more particularly coating the afore-mentioned materials is always difficult.

As a result, special means are needed to destroy the thin oxide layers which form spontaneously, even in surroundings which are slightly oxidising.

Various methods and processes of pickling zirconium and its alloys (e.g. zircalloy) have been used in order to eliminate passivation, but the deposits subsequently obtained on the metals are always insufficiently adherent and become detached if the treated parts have to be used at a high temperature or are subjected to periodic temperature changes.

To obviate or reduce the afore-mentioned disadvantage, the invention provides a novel surface treatment method which can give zirconium or zirconium alloy surfaces free from oxides so as to permit a chemical reaction between the substrate and a subsequent deposit in addition to the normal physical anchorage.

According to the invention, the workpieces of zirconium and its alloys are first pickled and then immersed in a bath of molten $CuCl_2$ in an inert atmosphere at a temperature between 430° and 600°C for a time between 10 seconds and 20 minutes.

The immersion times depend on the bath temperature.

The copper salts which are deposited on the surface of the work-pieces immersed in the bath protect them against any oxidation when they are taken out of the furnace in which the bath is disposed.

When zirconium and its alloys are immersed in molten $CuCl_2$, an exchange reaction occurs in which the zirconium is attacked by the chlorine and the reduced copper forms a compact deposit on the work-piece. The passivation layer does not offer protection at the operating temperature and is easily destroyed. Furthermore, because of the high temperature of the bath, the copper reacts with the zirconium to form a thin inter-penetration zone made up of the compound Zr—Cu.

The thickness of the copper film can be from 5 to 10μ; it is very compact and strongly anchored. When it leaves the bath, the copper is covered by mixtures of chlorides, but these salts can be removed by suitable surface treatment. The treatment can be performed e.g. with 10—15% by weight aqueous NH_4OH solutions at 80—90°C. The best results are obtained by immersing the coated work-pieces in a bath containing LiCl—KCl eutectic at 500°C for 8—10 seconds. The treatment dissolves surface chlorides which are difficultly soluble in water and leaves traces of lithium and potassium chloride on the work-pieces, which can easily be cleaned by washing in running water.

The copper deposits can be directly plated with various metals, using known methods of coating the copper. The following metals can easily be deposited on work-pieces prepared as aforesaid, with satisfactory results: Ni, Au, Ag, Cr, Cd, Pb, As and Sb by electrolysis, and Nb, Mo, W, by re-

duction of their halides in the gaseous phase.

A non-limitative example of the method according to the present invention will now be given by way of illustration.

Strips of zirconium with 99.8% purity and strips of Zircaloy-2 were pickled in a bath of the following composition:

HF	... ...	10% by volume
HNO_3	... ...	60% by volume
H_2O	... ...	30% by volume

The strips were immersed and stirred in a bath containing molten $CuCl_2$ for 2 minutes at 500°C. A current of argon supplied an inert atmosphere over the bath. The strips, after being taken out of the bath, were immersed for 8 seconds in the KCl—LiCl eutectic at 500°C. After being taken out and washed in running water, the work-pieces were coated partly with nickel and partly with chromium in baths used in industry. A micrographic examination showed a continuous, uniform copper film approximately 8μ thick. The work-pieces were then subjected to periodic temperature changes from 400°C to 20°C at a frequency of 4 changes per hour. They were examined after 240 temperature cycles but the deposits showed no sign of becoming detached.

WHAT WE CLAIM IS:—

1. A method for the surface treatment of zirconium and its alloys by chemical displacement, characterised in that the work-piece for treatment is first pickled and then immersed in a bath of molten $CuCl_2$ in an inert atmosphere at a temperature between 430° and 600°C for a time between 10 seconds and 20 minutes, in order to obtain a copper deposit which has partially reacted with the substrate.

2. A method of treatment according to claim 1, characterised in that the treated work-piece is given a further surface treatment which comprises immersing the work-piece in a bath containing LiCl—KCl eutectic at a temperature of 500°C for 8—10 seconds in order to dissolve salts which have adhered to the copper deposit.

3. The method for the surface treatment of zirconium and its alloys with copper substantially as herein described.

4. The method according to any one of the preceding claims and including the further step of plating a metal onto the treated surface.

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